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We have studied thin films composed of thin and thick wall template synthesized polypyrrole microtubules. We observe a crossover from three to one dimensional variable range hopping in our samples at low temperatures. Our results clearly indicate that the geometry of the microtubules has an influence on the conductivity. The transition temperature from 3 to 1 dimensional variable range hopping shifts to lower temperatures when high pressure is applied. The results are discussed on the basis of the geometry of the microtubules.

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HIGH PRESSURE CONDUCTIVITY STUDY OF TEMPLATE SYNTHESIZED POLYPYRROLE: OBSERVATION OF A CROSSOVER FROM THREE TO ONE DIMENSIONAL VARIABLE RANGE HOPPING

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ABSTRACT

We have studied thin films composed of thin and thick wall template synthesized polypyrrole microtubules. We observe a crossover from three to one dimensional variable range hopping in our samples at low temperatures. Our results clearly indicate that the geometry of the microtubules has an influence on the conductivity. The transition temperature from 3 to 1 dimensional variable range hopping shifts to lower temperatures when high pressure is applied. The results are discussed on the basis of the geometry of the microtubules.

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1. INTRODUCTION

Over the last decade several classes of highly conducting organic polymers have been discovered which may provide a viable alternative to conventional conductors in certain applications (Reynolds et al. 1989). These materials have a highly anisotropic quasi-one dimensional structure, which makes them fundamentally different from conventional inorganic metals. They have, however, the attractive feature that their conductivity is easily varied over several orders of magnitude by the addition of dopants.

The most severe problems limiting their wide use are their limited processibility and air stability. The prototypical conducting polymer is doped polyacetylene. Unfortunately the conductivity of both doped and undoped polyacetylene degrades rapidly on exposure to atmospheric oxygen. Polyacetylene is also completely insoluble and infusible, which renders it very difficult to process.

The conducting polymers polypyrrole and polyaniline are insensitive to oxygen. This fact in combination with the development of solutions of the problem of processing polypyrrole and polyaniline makes them attractive alternatives to polyacetylene. Various solutions of processing polypyrrole and polyaniline have been reported (Armes and Vincent 1987; Armes et al. 1987, 1989; Armes and Aldissi 1989, 1990; Armes et al. 1990; Sariciftci et al. 1994; Cai and Martin 1989; Cai et al. 1991; Martin et al. 1993 [a], [b]). One of these approaches uses the concept of synthesizing electronically conductive polymers within the pores of microporous host membranes (Cai and Martin 1989; Cai et al. 1991; Martin et al.1993 [a], [b]). The host membranes employed have cylindrical pores of uniform diameter. They called this method "*template synthesis*", because the pores act as

templates for the nascent conductive polymer. As a result of this templating effect hollow conductive polymer microtubules are obtained. The outside diameter and the length of these microtubules are determined by the pore diameter and the thickness of the membrane (typically 10 μm), respectively. The inside diameter, however, can be varied at will by varying the polymerization time. The microtubules can be freed by simply dissolving the template membrane (Cai and Martin 1989; Cai et al. 1991, Martin et al. 1993 [a], [b]).

The nanoscopic conductive microtubules show a higher degree of molecular and supermolecular order than is present in the same polymer when it is synthesized by more conventional methods (Cai et al. 1991, Martin et al. 1993 [a], [b]). In particular, the polymer chains in these microtubules are highly aligned (Cai et al. 1991). As a result of this enhanced order the template synthesized microtubules have higher electronic conductivities than conventional forms of these polymers (Liang and Martin 1990; Cai et al. 1991, Martin et al. 1993 [a]).

We have investigated the temperature dependence of thin films composed of template synthesized polyaniline and polypyrrole microtubules (Spatz et al. 1994). Depending on the diameter of the microtubules we found a crossover from three to two dimensional variable range hopping. We have suggested an explanation for this crossover based on the geometry of the microtubules. We also pointed out that a stringent test of our explanation of the crossover would be provided by measurements on 400 nm diameter microtubules with a controlled wall thickness. Furthermore the application of high pressure should also provide some insights and a test of our explanation.

In this paper we report the results of our temperature - pressure study of the conductivity of thin films composed of 400 nm hollow polypyrrole microtubules

with variable wall thickness.

2. EXPERIMENTAL

Nuclepore polycarbonate filters with pore diameters of 400 nm were used as the template membranes for the synthesis. Polypyrrole was synthesized within the pores of these membranes using conventional oxidative polymerization (Cai and Martin 1989; Cai et al. 1991; Martin et al. 1993 [a], [b]). Fig. 1 shows a schematic picture of the host membrane and the polymer microtubules growing in them. The wall thickness depends on the time of synthesis. The resulting geometric structure, shown in Fig. 2, can be controlled at will and is characterized by three parameters: (i) the diameter, d_f (as given by the pore diameter of the membrane); (ii) length, L (determined by the thickness of the membrane); (iii) wall thickness, d_w (controlled by the time of synthesis). The electronic structure is determined by the degree of doping and the molecular structure of the dopant (counterion). We used paratoluenesulfonate as a dopant and have achieved doping levels of 30 %.
After synthesis the microtubules were freed from the template membrane, collected on filter paper and compacted in a pellet press to yield tubule-based thin films (Martin et al. 1993 [a]).

Films with a thickness ranging from 2 to 4 μm composed of 400 nm hollow microtubules with varying wall thickness have been investigated. The microtubules are randomly oriented within the films. Four probe conductivity measurements were made by evaporating four Au contacts onto the film surface and attaching 0.03 mm diameter Pt wires using silver paint. Film resistance was measured using a constant voltage (maximum 20 mV excitation voltage) AC (16Hz) resistance bridge from Linear Research Corp. A k-type thermocouple (300 K to 40 K) and a

germanium resistor (below 40 K) were used for temperature measurements. The films had room temperature conductivities between 5 and 70 Ω^{-1} cm^{-1}. Rectangular shaped samples (7 x 3 mm^2) were placed in a beryllium copper high pressure clamp cell (Chu et al. 1968) which allowed to generate hydrostatic pressures up to 2 GPa. Fluorinert, FC-77, was used as a pressure medium. The high pressure cell fits into a helium cryostat, allowing measurements in the temperature range from 300 K to 1.2 K.

3. RESULTS AND DISCUSSION

Conducting polymers are a prototype of disordered conductors, where the disorder is caused by topological defects, impurities, chain length variation, noncrystallinity, etc. Their conductivity, σ, is described by the ***Mott Variable Range Hopping (MVRH) model*** of disordered systems. At sufficiently low temperatures σ is determined by the thermally activated hopping over variable distances. The conductivity is then given by

$$\sigma \propto T^{-1/2} \exp[-(T_0/T)^n], \quad n = 1/(1 + D) \qquad (1)$$

where D is the dimension of the conduction process (Mott and Davis 1979; Mott and Kaveh 1985; Apsley and Hughes 1974, 1975). The *Mott temperature*, T_0, is a function of the localization length, l, and the density of states at the Fermi level, $N(E_F)$.

$$T_0 \propto l^{-D} N(E_F)^{-1} \qquad (2)$$

Another important quantity of the MVRH model is the average hopping distance, R_h, which increases with decreasing temperature according to

$$R_h/l \propto (T_0/T)^n \qquad (3)$$

The electrical conductivity of our films composed of template synthesized hollow 400 nm diameter microtubules with variable wall thickness is described by equ. 1 of the MVRH model. Since the conduction process in many conducting bulk polymers follows the MVRH model (Sato et al. 1991; Meikap et al. 1993; Reghu et al.1993), we conclude that the conductivity of template synthesized polypyrrole is determined by the **intratubulus** conduction. We have to take into account, however, that the density of compressed films composed of microtubules is smaller than that of bulk material. This may explain the fact that we observe a stronger increase of the resistance with decreasing temperature (about 10 orders of magnitude compared to 5-6 orders in conventionally prepared polypyrrole (Meikap et al. 1993; Reghu et al. 1991) from 300 to 4 K). Fig. 3 shows the temperature dependence of the resistance of a sample composed of thick walled microtubules (synthesis time: 300 sec, wall thickness: 60 nm) in the temperature range from 123 K - 16 K (a) and between 16 K - 4 K (b) . *It is important to notice that the resistance changes by about 5 orders of magnitude in the temperature range from 123 K - 16 K and about 6 orders of magnitude in the temperature range from 16 K - 4 K.* This large resistance change is an **essential** point, because distinguishing between $T^{-1/2}$, $T^{-1/3}$, or $T^{-1/4}$ dependence would be **impossible** if data were not collected over a large resistance range. In the high temperature range (Fig. 3 a) the exponent n is equal to 1/4, indicating that 3 D variable range hopping takes place. In the low temperature range (Fig. 1 b) the exponent n is equal to 1/2, indicating that the conduction process is now one dimensional. Although the validity of the MVRH model in **one** dimension is still discussed, these results in combination with the previous ones (Spatz et al. 1994) support strongly the transition to a preferably 1 D conduction. The change of the dimensionality of the conduction at about 16K

and the quality of the fits of equ. 1 to our data is most convincingly demonstrated in Fig. 4. There we have plotted the difference $\ln(R_{exp}) - \ln(R_{fit})$ of the experimentally measured resistance value (R_{exp}) and the resistance value (R_{fit}) determined by fitting the data to equ. 1. Ideally this value should be zero. It can be seen that the difference fluctuates around zero ***only*** for the n = 1/2 and n = 1/4 fits in the low temperature and high temperature range, respectively. Thus supporting ***unambiguously*** our claim. We have chosen this representation over (dlnR/dlnT) versus T (Zabrodskii et al. 1984, Rosenbaum 1991), because it allows an exacter determination of the transition temperature, due to the fact that the scattering of the data points are less important in our representation.

Fig 5 shows the temperature dependence of the resistance of samples composed of hollow thin wall polypyrrole microtubules (synthesis time: 30 sec, wall thickness: 20 nm) in the temperature range from (a) 200K - 40 K, and (b) and 60K - 13 K.,

Again we see a similar behavior of the temperature dependence of the resistance as in the case of the samples composed of thick wall microtubules. The plot of $\ln(R_{exp}) - \ln(R_{fit})$ shown in Fig. 6 confirms this statement. It is important to notice, however, that the crossover temperature occurs at a higher temperature (~ 50 K).

The change in the exponent of the conduction process could be explained by (i) Coulomb interaction of the charge carriers, and (ii) crossover from 3D to 1 D conduction:

(i) Equ. 1 is valid, if the density of states, $N(E_F)$ is almost constant at low temperature. At very low temperature the Coulomb interaction between charge carriers reduces $N(E_F)$ resulting in the *Coulomb gap* at T = 0 K (Efros and Shklovskii 1975). This effect changes the temperature dependence

of the conductivity, so that even for 3 D hopping the exponent n has a value of 1/2.

(ii) The average hopping distance, R_h, increases with decreasing temperature (equ. 3). The finite wall thickness, d_w, restricts, however, the radial hopping in our samples, which would result in a crossover to 2 D conduction (Spatz et al. 1994). If R_h exceeds finally a certain value of the order of the diameter of the microtubules the hopping is forced into the direction along the microtubulus axis, resulting in a 1 D hopping process.

The explanation based on the existence of a Coulomb gap at low temperatures is unlikely because of two reasons. Firstly, it should be expected at very low temperatures only. Secondly, the charge carriers in polypyrrole are bipolarons and their Coulomb repulsion is screened to a large extent by the deformation potential. Furthermore, if the change of the exponent could be explained by a Coulomb gap, then it is expected according to the Castner criterion (Rosenbaum 1991) that the ratio of the characteristic temperatures $T_H/T_L \approx 80$. Here T_H and T_L correspond to the Mott temperature in the high and low temperature region, respectively.

In our experiments we find a ratio which is an order of magnitude larger (500 - 800). This supports our conclusion that the transition is not due to the existence of a Coulomb gap at low temperatures.

If the geometry of the microtubules is responsible for the dimensional change of the hopping process a change of the average hopping distance should lead to a shift of the crossover temperature. Such changes of the average hopping distance can be achieved , for example, by the application of high pressure, of a magnetic field, or by a change of the molecular or supermolecular order.

If we compare the data for the thin and thick wall microtubules, we find a

decrease of T_0 with increasing wall thickness. According to equ. 3 this results in a decrease of R_H, if the change in the localization length does not compensate this effect. Our results show a shift of the crossover temperature to lower temperatures if the wall thickness increases supporting our suggestion that the geometry of microtubules plays an important role in the 3 D to 1 D crossover.
Unfortunately the experimental determination of T_0 allows only the determination of the ratio of the hopping distance, R_H, and the localization length, l. Therefore only this qualitative discussion is possible at the moment. We plan, however, to perform additional magnetoresistance measurements, which will allow us to determine the localization length, and therefore provide the means for a quantitative discussion.

Based on this explanation one should also expect an intermediate temperature range where the hopping takes place in 2 dimensions in the mantle of the tubules. Of course, we can find a narrow temperature range where we see a slope of 1/3 in the Mott plot. However, we believe that this temperature range is too narrow for reliable fits of the data to equ. 1. Nevertheless, we have observed 2 D conduction over a ***wide*** temperature range in 100 nm diameter and 50 nm diameter polyaniline and polypyrrole microtubules, respectively (Spatz et al. 1994).

Further support is provided by the results of our high pressure study, shown in Figs. 7 and 8 for samples composed of thick wall microtubules and Figs. 9 and 10 for samples composed of thin wall microtubules. It can be seen that the crossover temperature shifts to lower values (16 K → 5 K for the thick wall sample, and 50 → 30 K for the thin wall sample). This in turn would agree with our explanation, that 3 D to 1 D transition is due to the geometry of the microtubules, if

the average hopping distance decreases with pressure.

In Fig. 11 we have plotted the pressure dependence of the Mott temperature, T_0, for the thick wall and thin wall sample. We see that T_0 decreases by more than 80% at 2 GPa. This fact indicates that the application of pressure leads to a decrease of the hopping distance. This in turn shifts the 3 D - 1 D crossover temperature to appreciably lower values. In other words 3 D conduction is favorized under pressure. This is exactly what we have found and supports therefore our explanation.

As a final result we show in Fig. 12 the pressure dependence of the room temperature conductivity of both samples. It can be seen that the application of pressure increases the room temperature conductivity by a factor of 2 - 3, a factor which agrees well with those found in bulk polypyrrole (Lundberg et al. 1985; Maddison et al. 1988; Maddison et al. 1989; Lundin et al. 1990)

SUMMARY

We have shown that template synthesized conducting polymers provide an excellent model system for investigating size effects on a submicron scale on the hopping conduction of localized charge carriers. The special technique of synthesis allows to produce films composed of polymer microcylinders with well defined diameter, length, and wall thickness. The electrical conductivity of these films is determined by the variable range hopping of localized charge carriers in the wall of the polymer microtubulus. The dimension of the conduction process changes from 3 D to 1 D when the average hopping distance exceeds a certain critical value related to the geometry and size of the microtubules. Hydrostatic pressure strongly affects the electrical properties. The room temperature conductivity increases by a

factor 2 - 3. The characteristic Mott temperature describing the slope of the conductivity versus temperature curve, decreases by more than 80% at 2 GPa, resulting in a decrease of the average hopping distance. It also shows that 3 D conduction is favored by hydrostatic pressure.

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FIGURE CAPTIONS

Fig. 1. Schematic picture of the host membrane with polymer tubulus

Fig. 2. Schematic picture of the polymer microtubulus; d_f: diameter, L: length, d_w: wall thickness

Fig. 3. Temperature dependence of the resistance of samples composed of hollow thick wall polypyrrole microtubules (d_w = 60 nm) in a) the temperature range from 123 K - 16 K, and b) the temperature range from 16 K - 4 K.

Fig. 4. $\ln(R_{exp}/R_{fit})$ versus temperature for the thick wall samples.

Fig. 5. Temperature dependence of the resistance of samples composed of hollow thin wall polypyrrole microtubules (d_w = 20 nm) in a) the temperature range from 200 K - 40 K, and b) in the temperature range from 60 K - 13 K.

Fig. 6. $\ln(R_{exp}/R_{fit})$ versus temperature for the thin wall samples.

Fig. 7. Temperature dependence of the resistance of samples composed of hollow thick wall polypyrrole microtubules (dw = 60 nm) at a pressure of 1.5 GPa in a) the temperature range from 70 K - 4 K, and b) the temperature range from 6 K - 1.2 K.

Fig. 8. $\ln(R_{exp}/R_{fit})$ versus temperature for the thick wall samples at 1.5 GPa.

Fig. 9. Temperature dependence of the resistance of samples composed of hollow thin wall polypyrrole microtubules (dw = 20 nm) at a pressure of 1.5 GPa in a) the temperature range from 123 K - 24 K, and b) the temperature range from 60 K - 6 K.

Fig. 10. $\ln(R_{exp}/R_{fit})$ versus temperature for the thin wall samples at 1.5 GPa

Fig. 11. Pressure dependence of the Mott temperature, T_0, of a) thick wall , and b) thin wall samples.

Fig. 12. Pressure dependence of the room temperature conductivity of thick (○) and thin (□) wall samples